# Groundwater Pollution by Nitrates from Livestock Wastes

## by V. M. Goldberg*

Utilization of wastes from livestock complexes for irrigation involves the danger of groundwater pollution by nitrates. In order to prevent and minimize pollution, it is necessary to apply geological-hydrogeological evidence and concepts to the situation of wastewater irrigation for the purposes of studying natural groundwater protectiveness and predicting changes in groundwater quality as a result of infiltrating wastes. The procedure of protectiveness evaluation and quality prediction is described. With groundwater pollution by nitrate nitrogen, the concentration of ammonium nitrogen noticeably increases. One of the reasons for this change is the process of denitrification due to changes in the hydrogeochemical conditions in a layer. At representative field sites, it is necessary to collect systematic stationary observations of the concentrations of nitrogenous compounds in groundwater and changes in redox conditions and temperature.

## Introduction

At the present time, nitrates are the most widespread pollutants of groundwater. In many instances this is due to human activity, particularly the intensification of agriculture. Accumulation of nitrates in humans is associated with methemoglobinemia, an especially serious disease in a newborn child. Nitrates and nitrites have also been shown to be transformed *in vivo* to N-nitroso compounds (*1*).

One of the main sources of groundwater pollution by nitrates is livestock breeding, particularly because of the changeover from small single farm operations to large centralized livestock breeding complexes. Huge amounts of waste (manure) are piled up at these agricultural-industrial complexes and their reuse is a complicated problem. One of the methods of utilization is for spray irrigation in diluted form. With this method, however, there is a danger of groundwater pollution. Therefore, natural groundwater protectiveness and possible change of its quality as a result of wastewater infiltration from the ground surface should be considered when determining the areas for irrigation with livestock wastes.

## Pollutants

Livestock waste components that pollute groundwater are nitrogen, phosphorus, potassium, and microorganisms. At the same time, nitrogen, phosphorus, and potassium are nutrients for plants. Phosphorus is nearly completely retained by the soil layer and, for all practical purposes, does not reach the groundwater table. Potassium is also retained by the soil and rocks in the zone of aeration, though to a lesser extent than phosphorus, forming cation complexes adsorbed to soils and rocks.

Microorganisms (bacteria of the coliform bacillus group, pathogenic enterobacteria, etc.) are a serious danger to humans. However, because their lifetime is relatively short, aquifer bacterial pollution is generally localized to a small area that is in close proximity to the source of the pollution (*2,3*).

The main polluting components of livestock wastes are nitrogenous compounds. Of these, nitrates are of greatest concern. Nitrogen occurs in groundwater mainly in three forms: nitrates, nitrites, and as the ammonium ion. Their participation in groundwater pollution is unequal. Ammonium and nitrite ions are intermediate and unstable forms of nitrogen in oxidization processes that produce the more stable forms of nitrogen as nitrate. Especially unstable among these forms of nitrogen are nitrites which are readily oxidized into nitrates in the zone of aeration and are practically absent in groundwater or occur at very low concentrations. Ammonium cations are also readily oxidized. Furthermore, they are well adsorbed by soil constituents and rocks according to a cation exchange mechanism. Nevertheless, ammonium nitrogen occurs in groundwater rather often and its concentration may be substantial under reductive conditions or in situations when conditions are in transition from oxidative to reductive.

The final products of the nitrification process are nitrates. They are characterized by relative stability, low adsorptivity, and high migration capacity. Accumula-

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tion of nitrates in groundwater and their widespread occurrence are the result of these characteristics.

Simultaneously with nitrification, the process of denitrification takes place in groundwater, resulting in reduction of nitrates to ammonium ions with subsequent release of ammonia and free nitrogen. Denitrification is an important process because it determines the forms of nitrogenous compounds occurring in groundwater, a peculiarity of groundwater nitrate pollution. Denitrification is enhanced by a change of redox conditions of an aquifer in the direction of reduction.

Reductive conditions often take place in the zones of slow water exchange. Ammonium nitrogen finding its way into these zones from the ground surface remains in this form for a long time and is not oxidized to nitrate nitrogen. Alternatively, nitrate nitrogen is reduced to ammonium nitrogen under these conditions. Ammonium nitrogen pollution of groundwater may remain or develop in such aquifers (3,4).

Nitrate reduction also takes place when ferrous iron is oxidized to ferric iron at the expense of oxygen in nitrates. Likewise, reduction of nitrates may be promoted by oxidation of organic substances and sulfur which are present in groundwater. Therefore, when monitoring nitrate nitrogen and ammonium nitrogen concentrations in groundwater it is very important to control redox conditions and to measure the content of organic substances, iron, and sulfur in groundwater.

# Groundwater Protectiveness

Aquifers occurring near the ground surface and particularly phreatic aquifers are most susceptible to nitrate pollution as well as to other types of manmade pollution. In the case of irrigation by livestock wastes, the main pollution load falls on groundwater. That is why the conditions of natural groundwater protectiveness should be considered and estimated when selecting the areas for irrigation by livestock wastes. The estimation procedure has been developed by us and presented in the literature (5,6). The purpose of this method is to determine how vulnerable or susceptible an aquifer is to contamination by activities occurring on or near the surface.

Natural groundwater protectiveness is understood as the combination of geological-hydrogeological features of the aquifer that hamper or prevent penetration of pollutants. The main factor of groundwater natural protectiveness or the main geological feature that protects the aquifer is the presence of overlying semipermeable deposits.

Deposits are considered semipermeable if their permeability coefficient is less than 0.1 m/day. Loamy sands, sands with clay, and clays are soil types that belong to this category.

The first step in determining the protectiveness of a particular aquifer is to assign numerical values for important aquifer characteristics. Then these individual contributions are added together to give a cumulative sum. The greater the magnitude of the sum, the higher

the protectiveness of the aquifer. The complex of features characterizing the conditions of groundwater protectiveness are as follows: depth of groundwater table (or thickness of the zone of aeration); thickness of semipermeable deposits in the profile of the zone of aeration; and lithology and permeability properties of semipermeable deposits (lithology and permeability properties are interrelated). The summation, depending on these three features, is determined using Tables 1 and 2.

There are five gradations of depth (H) of the groundwater table (Table 1): < 10 m, 10–20 m, 30–40 m, > 40 m. The first gradation with minimum depth of groundwater table (H < 10), corresponds to number 1; the second gradation, to number 2; the third, number 3; the fourth, number 4; and the fifth, number 5. These numbers are set up on the condition that the zone of aeration is composed of uniform sandy soils.

The thickness of semipermeable deposits ($m_o$) can be subdivided into 11 gradations (Table 2): < 2 m, 2–4 m, ... 18–20 m, and > 20 m. There are three groups of semipermeable deposits that can be distinguished in Ta-

**Table 1. Depths (H) of groundwater table and corresponding numbers.**

| H(m) | $\leq 10$ | $10 < H \leq 20$ | $20 < H \leq 30$ | $30 < H \leq 40$ | $> 40$ |
|---|---|---|---|---|---|
| Numbers | 1 | 2 | 3 | 4 | 5 |

**Table 2. Thickness ($m_o$) and groups of rocks (a,b,c) of semipermeable deposits and corresponding numbers.**

| $m_o$, m | Rock | Numbers |
|---|---|---|
| < 2 | a | 1 |
|  | b | 1 |
|  | c | 2 |
| $2 < m_o \leq 4$ | a | 2 |
|  | b | 3 |
|  | c | 4 |
| $4 < m_o \leq 6$ | a | 3 |
|  | b | 4 |
|  | c | 6 |
| $6 < m_o \leq 8$ | a | 4 |
|  | b | 6 |
|  | c | 8 |
| $8 < m_o \leq 10$ | a | 5 |
|  | b | 7 |
|  | c | 10 |
| $10 < m_o \leq 12$ | a | 6 |
|  | b | 9 |
|  | c | 12 |
| $12 < m_o \leq 14$ | a | 7 |
|  | b | 10 |
|  | c | 14 |
| $14 < m_o \leq 16$ | a | 8 |
|  | b | 12 |
|  | c | 16 |
| $16 < m_o \leq 18$ | a | 9 |
|  | b | 13 |
|  | c | 18 |
| $18 < m_o \leq 20$ | a | 10 |
|  | b | 15 |
|  | c | 20 |
| > 20 | a | 12 |
|  | b | 18 |
|  | c | 25 |

ble 2 on their lithology and hence on their permeability properties: group a, loamy sands, sandy loams (permeability coefficient of 0.1–0.01 m/day); group b, loams, sandy clays (permeability coefficient of 0.01–0.001 m/day); and group c, clay loams, clays (permeability coefficient of less than 0.001 m/day).

The summation ($\Sigma$) stipulated by gradations of depth of the groundwater table and by the thickness of semipermeable deposits and their lithology defines the degree of groundwater protectiveness. Six categories of groundwater protectiveness can be distinguished according to the magnitude of the summation: I, $\Sigma \leqslant 5$; II, $5 < \Sigma \leqslant 10$; III, $10 < \Sigma \leqslant 15$; IV, $15 < \Sigma \leqslant 20$; V, $20 < \Sigma \leqslant 25$; VI, $\Sigma > 25$. Summations that satisfy the conditions of category I are the worst from the point of view of protectiveness. The best conditions for protectiveness of aquifers are category VI.

Categories V and VI may be referred to as groundwaters that will be relatively protected from nitrate penetration; however, this distinction mostly applies to category VI; categories III and IV, poorly protected groundwater; and categories I and II, unprotected groundwater. On the whole, groundwater in unconfined or phreatic aquifers in contrast to groundwater in confined aquifers is characterized by low protectiveness. On this basis, mapping of a region to determine areas that are more vulnerable to pollution, e.g., areas with low groundwater protectiveness, can be performed.

## Prediction of Concentration Changes

When spray irrigation with livestock waste waters is carried out, some of the nitrates penetrate through the zone of aeration and reach groundwater, causing pollution. A mass balance for nitrogen in irrigation waters that are applied to fields is characterized by the following:

$$V = V_p + V_r + V_n + V_B \qquad (1)$$

where V is the total amount of nitrogen in all forms applied to fields annually; $V_p$ is the amount of nitrogen assimilated by plants; $V_n$ is the amount of nitrogen remaining in the zone of aeration including soil; $V_r$ is the nitrogen loss in gaseous form; and $V_B$ is the amount of nitrogen reaching the groundwater table. It is necessary to know, or be able to estimate, $V_p$ in order to predict groundwater pollution under irrigation fields.

According to the data presented in the literature and summarized in reviews (4,7–10), certain components of the nitrogen mass balance vary over a wide range, depending on the type of soil, type of agricultural planting, irrigation regime, and climatic conditions. Thus, the amount of nitrogen that is assimilated by plants varies from 15 to 60%, but for the most part, it ranges from 40 to 50%. Nitrogen losses in gaseous form range from 4 to 10% to 50 to 65%, with an average of 20 to 30%. Of the applied nitrogen, 10 to 20% remains in the zone of aeration, as well as in the soil. Of the applied nitrogen,

5 to 15% reaches the groundwater table, with an average of 10% of the total amount of nitrogen applied to fields along with livestock wastes. The given values of the nitrogen balance components are very tentative, but they give an indication of the orders of magnitude. Thus, it may be estimated that $V_B = 10\%$. In each particular case, however, this value should be refined.

In the mass balance calculation, it has been assumed that the irrigation field has a rectangular form with sides L and S; side L coincides with the direction of natural groundwater flow. The rate of natural groundwater flow is $V_e = k \times i_e$, where k is the permeability coefficient, and $i_e$ is natural flow gradient. The average aquifer thickness is m, the porosity of water-bearing rocks is n, and background (natural) pollution (nitrates) of groundwater is $C_o$.

The field is irrigated by wastes annually throughout the entire vegetation period. Irrigation is applied several times at specified intervals. The total volume of applied wastes is W. To simplify calculations, repeated irrigation is substituted by one-time irrigation. The difference between the results of calculations of nitrogen concentrations in groundwater for a one-time irrigation and a two-time irrigation was shown to be negligible.

The duration of such equivalent one-time irrigation is identical to the sum of the separate irrigation periods. The volume (W) of wastes applied to the fields equals the sum of the volumes applied in different periods. The time from the end of the irrigation period in the current year until the beginning of the irrigation period in the following year is the nonirrigation period $t_M$.

From experience with irrigation system operation, it is assumed that the volume of irrigation water $W_B$ penetrating to the groundwater table amounts to 10 to 30% of annual water application and depends on environmental conditions (7,11,12). For calculation, it is assumed that $W_B = 30\% W$. The average concentration of pollutants (nitrates) in applied wastes reaching the groundwater table is $C_B$. The value of $C_B$ is determined as a ratio of $V_B$ to $W_B$.

The scheme of calculation of groundwater mineralization is the following. In the irrigation period, wastes used for irrigation infiltrate and mix with the groundwater volume underlying the irrigation field and produce polluted groundwater in a layer. In a nonirrigation period, this water is moved downstream by pure water. In the next irrigation period, infiltrating wastes mix anew with groundwater under the irrigation field, but now it consists of two components: groundwater polluted in the first period and pure groundwater that partially replaced polluted groundwater during the nonirrigation period. This process continues in subsequent irrigation and nonirrigation periods. Polluted groundwater may also be diluted by precipitation.

In the case of one-time irrigation, the calculational relationship for the prediction of pollutant concentration changes with time under the irrigated area and has the form (4,5):

$$C_j = \frac{W_B \cdot C_B + W_o' \cdot C_{j-1} + W_o'' \cdot C_o}{W_o + W_B} \qquad (2)$$

where $C_j$ is the concentration of pollutants in groundwater under irrigated areas at any j-year after the beginning of irrigation; $C_{j-1}$ is the concentration of pollutants in groundwater in the preceding year; $W_0$ is the total volume of groundwater under the irrigated area; $W_o = L \cdot S \cdot m \cdot n$; $W'''$ is the volume of pure water which partially replaces polluted groundwater during the nonirrigation period; $W_o'' = S \cdot m \cdot n \cdot x_M$; $x_M = V_e \cdot t_M/n$; and $W_o'$ is the volume of polluted groundwater remaining under the irrigated area after replacement by pure water during the nonirrigation period, $W_o' = S \cdot m \cdot n(L - x_M)$.

The concentration of pollutants after the irrigation period in the first year of irrigation is:

$$C_1 = \frac{W_0 \cdot C_0 + W_B \cdot C_B}{W_0 + W_B} \qquad (3)$$

A peculiarity of calculations with Eq. (2) is the following. Pollution concentration in groundwater for the next year is determined from the concentration of the preceding year. Therefore, to predict pollution concentrations for year j after the beginning of irrigation, preliminary calculations should be made beginning with the first year of irrigation. For example, to determine the concentration for year 10 after the beginning of irrigation, it is necessary to know the pollution concentration in the preceding year, i.e., in year 9. After determination with Eq. (3) of the pollution concentration in the first year of irrigation, pollution concentrations for the second, the third, and the fourth (up to the required year) are determined one after another with Eq. (2).

Let us consider the change of pollution concentration in groundwater under the irrigation field with allowance for precipitation. Assume that the minimum amount of infiltrating annual precipitation in the irrigation field with the area F is $W_A = F \times H_{min} \times \epsilon$, where $H_{min}$ is the minimum annual precipitation, and $\epsilon$ is the infiltration coefficient. The concentration of pollutants (nitrates) in precipitation is $C_A$.

Pollution concentration in groundwater in year j after the beginning of irrigation is determined as follows:

$$C_j = \frac{W_B \cdot C_B + W_o' \cdot C_{j-1} + W_o'' \cdot C_0 + W_A \cdot C_A}{W_0 + W_B + W_A} \qquad (4)$$

After the first year of irrigation pollution, the concentration under the irrigation field is as follows:

$$C_1 = \frac{W_B \cdot C_B + W_0 \cdot C_0 + W_A \cdot C_A}{W_0 + W_B + W_A} \qquad (5)$$

In most cases, it may be assumed that $C_A \simeq 0$. Then Eq. (4) and (5) have the form:

$$C_j = \frac{W_B \cdot C_B + W_o' \cdot C_{j-1} + W_o'' \cdot C_0}{W_0 + W_B + W_A} \qquad (6)$$

$$C_1 = \frac{W_B \cdot C_B + W_0 \cdot C_0}{W_0 + W_B + W_A} \qquad (7)$$

Measuring units for terms appearing in Eqs. (4)–(7) are $C(g/l)$ and $W(m^3)$.

The calculation of concentrations using Eqs. (4)–(7) is analogous to that described previously. The increase in groundwater pollution concentration calculated by Eq. (2) is less than the value determined by using Eq. (4). This is due to groundwater dilution by infiltrating precipitation.

## Conclusion

Utilization of wastewater from livestock complexes, as well as municipal wastes for the purpose of irrigation, is an urgent problem. For hydrogeological substantiation of this problem from the point of view of groundwater protection, it is expedient to set up test field stations. These field stations should be set up to collect data under typical environmental conditions for stationary study of the changes in groundwater quality under the impact of irrigation and under conditions of migration and transformation of nitrogenous compounds in groundwater. These investigations should be of a complex nature, including the study of the hydrodynamics of the aquifer, its hydrochemical, redox and temperature conditions, and processes of interaction in the water-rock water-soil system.

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